CHEMICAL & ENGINEERING NEWS

C&EN

MARCH 9, 1992

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CHEMICAL & ENGINEERING NEWS

C&EN

MARCH 9, 1992

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LETTERS

Region V election

A question concerning the recent Region V board member election that was raised in a letter from E. Ann Nalley (C&EN, Jan. 20, page 2) needs clarification. Her statement is, "Also, even though our society has strict regulations about the use of society publications in campaigning, these are often difficult to enforce." We assume that this statement was made because of an announcement of the two nominees (namely, the cosigners of this letter) in a divisional newsletter prior to public knowledge that Nalley was a third candidate by petition. This omission was corrected, as far as possible, prior to the election by a separate mailing of statements by all three candidates—at the division's expense—to the divisional membership.

Two erroneous inferences could be drawn from the Jan. 20 letter. We want to make it clear that our society's major news publication, C&EN, was not involved. It could also have been inferred from the letter that one of us was somehow responsible. That is not the case. The short newsletter announcement was, in fact, written by a new assistant editor in the absence of the regular editor.

Both of us are grateful to our supporters, and we look forward to your further participation in furthering the society's goals through our respective ACS roles.

Clara D. Craver
ACS Councilor
John G. Verkade
Director, ACS Region V

Women in chemistry

The American Chemical Society at all levels is airing its strong commitment to increase the number and participation of women in chemistry. One cannot help but wonder about the sincerity of this commitment when one sees the major chemical conferences with zero invited female speakers. One example is the last (32nd) National Organic Symposium, June 16–20, 1991, at the University of Minnesota. There were 11 speakers, all male, and five presiding officers, all male.

Today I received the program for the 23rd National Medicinal Chemistry Symposium, which lists 22 invited speakers, again all male, zero female. I have decided to boycott it on this ground. I shall not expose myself anymore to the bigotry of the major speakers paying lip service to the oftentimes numerous female chemists on the acknowledgment slides of their talks, while using their own prestigious old-boy network to exclude these or other females from the scientific visibility of the major conferences.

Vera M. Kolb
Professor of Chemistry
University of Wisconsin, Parkside

Supercritical water

Although I found the article on supercritical water (C&EN, Dec. 23, 1991, page 26) an excellent discussion of theoretical investigations into supercritical water, I believe that the following clarifications are necessary to give your readers a complete picture of the status of this technology and its practical applications.

Stone & Webster Engineering Corp. has been involved in a cooperative agreement with the Department of Energy's Office of Industrial Energy Efficiency since 1988 to demonstrate a water oxidation process in an industrial application. Since 1989, the program has focused exclusively on demonstrating the supercritical water oxidation process developed by Modar Inc. of Natick, Mass. The Modar technology was selected for demonstration by a panel of industry representatives as being the most developed wet oxidation technology available that could achieve complete destruction of an organic waste.

During the course of our investigations, we discovered that the primary obstacle to commercial application of supercritical water oxidation was not a lack of fundamental data on the supercritical fluid or oxidation reaction kinetics. Volumes of this data have been obtained empirically, but are held as trade secrets by technology developers. Our work has shown that the primary obstacle is the observed plugging of the reactor system due to the generation of reaction products—primarily sodium salts that are insoluble in the supercritical fluid. These salts are encountered when treating most waste feeds containing chlorides, sulfates, and other constituents that form acids upon oxidation. So severe is this plugging problem, that reactor systems have plugged after only minutes of operation. It is interesting to note that nearly all hazardous-waste feeds will form sticky solids during treatment. To date, this phenomenon is not fully understood, nor has

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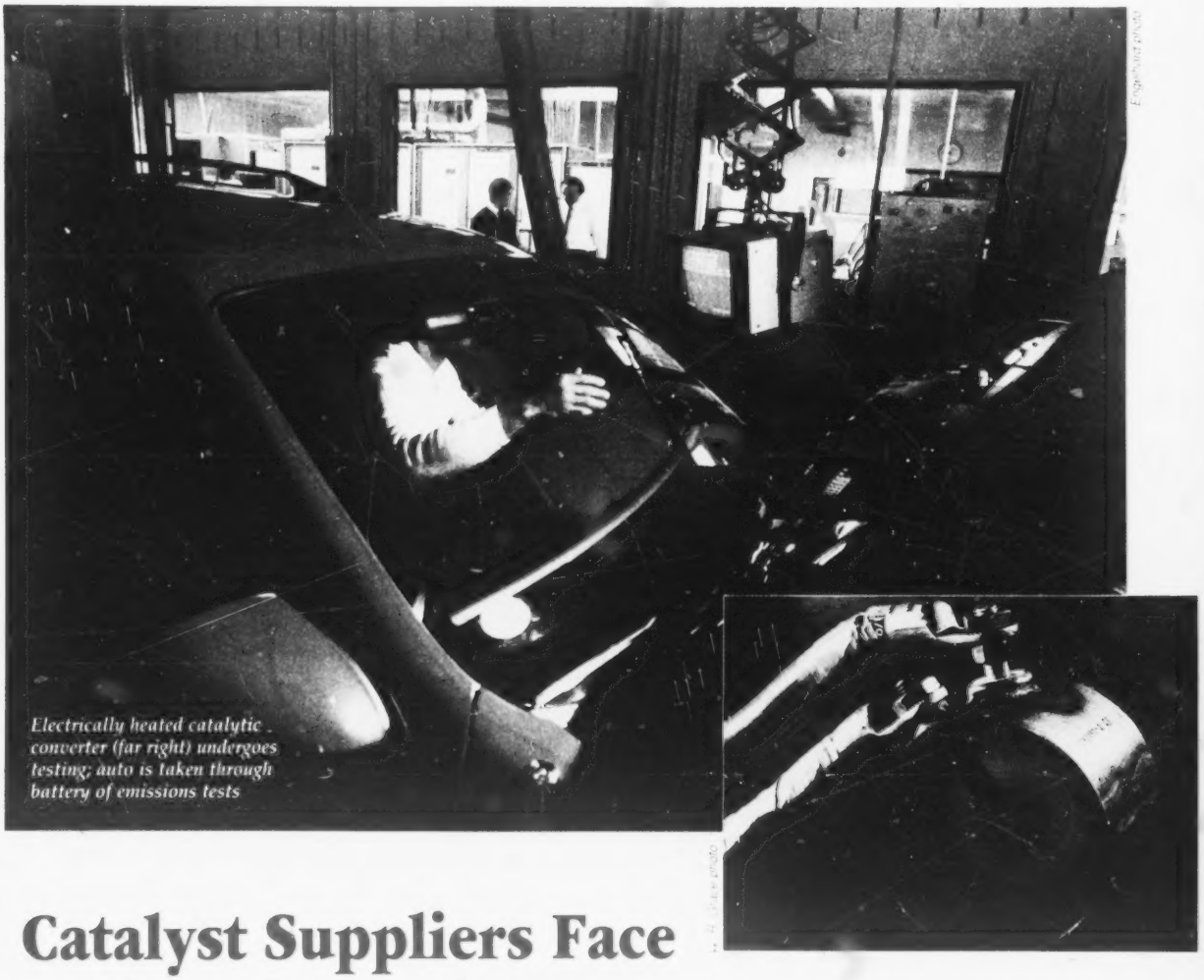

Electrically heated catalytic converter (far right) undergoes testing; auto is taken through battery of emissions tests

Catalyst Suppliers Face Changing Industry

Ann M. Thayer,
C&EN Northeast News Bureau

Catalyst suppliers and their customers are being pulled in many directions by economic and environmental forces. The three major catalyst markets—petroleum refining, chemical processing, and emissions control—are all facing economic, competitive, and regulatory pressures that have direct or indirect effects on markets. As a result, catalyst producers are being pushed to develop products with improved performance to meet changing environmental standards.

What has added to the complexity, challenge, and therefore opportunity in the industry is that environmentalists have not pointed a particular new fight at any one of these process developers. Rather, they have focused their attention on a variety of issues. Meanwhile, new technology is emerging. Unfortunately, not all of it is environmentally friendly. Every new application or development must be carefully considered in the context of existing technologies.

And new technology in the next decade will not succeed unless it takes that very much into account.

A catalyst supplier's success is rooted in its ability to respond to a variety of customer demands with the needed technological advances. Refiners are asking for cost-effective catalysts to meet the production requirements of reformulated gasoline and the automotive, process, and energy industries are looking for ways to reduce emissions. Catalysts also play a key role in chemical processes by controlling the rate and direction of reactions. Here catalyst suppliers are being asked to provide shorter cycles and lower-cost catalysts than those used in the past.

Technician researches use of catalyst in the production of polyurethane foam at Air Products laboratory

ucts, while maintaining production efficiencies.

Catalyst markets depend significantly on the prosperity of end-use markets for the products they make. The nearly $6 billion worldwide merchant catalyst market supports chemical processing and manufacturing industries that produce goods worth more than a hundred times that amount.

The worldwide market for catalysts is expected to grow about 4% per year during the next few years, according to Catalyst Group, a Spring House, Pa.-based commercial and technical consulting firm. An expanding aspect of the catalyst industry will be in the regeneration and recycling of used catalysts, explains Clyde Payn, president of Catalyst Group.

Most growth will be in Europe, in emissions catalysts, and the Pacific Rim, in catalysts for petroleum refining. Among the largest markets, the $1.6 billion European market for catalysts is projected to grow about 10% annually to $2.6 billion by 1995. Over 35% of catalysts sold worldwide, or $2.1 billion in 1990, were used in North America, based on figures from Catalyst Group. This market is expected to grow only about 4% to $2.5 billion by 1995. The North American catalyst market can be divided roughly into three segments of about equal size: petroleum refining, 35%; chemical processing, 31%; and environmental applications, 34%.

Changes in petroleum refining

No market for catalysts is in as dynamic a state of flux as that for petroleum refining catalysts. Catalysts used in refining fall into several general areas: fluid cracking catalysts (FCC), hydrocracking, reforming, isomerization, hydrotreating, and alkylation catalysts.

In the U.S., changes dictated by the 1990 Clean Air Act require new gasoline formulations; new catalysts will be needed to meet those requirements. This also must be accomplished in what producers see as a relatively short amount of time. As early as 1992 in some areas and by 1995 in many others, the Clean Air Act mandates reductions in gasoline volatility, and in benzene and other aromatics, and provides for an increase in oxygen content to reduce emissions. And, in less than two years, low sulfur and aromatics standards will be in effect for diesel fuels.

To produce the components of reformulated gasolines, the economics and roles of various refinery operations will move in different directions, influencing catalyst suppliers' products both positively and negatively. Catalyst suppliers must respond quickly with new catalysts, a move that will necessitate large R&D investments. The refining catalyst industry has been plagued by problems of overcapacity and falling prices for the past several years, along with continuing worldwide recession economics and lingering effects of the Persian Gulf War.

"The Gulf War created an artificially high demand for energy ... and that means a high demand for catalysts," says William Gustafson, group vice president and general manager of petroleum catalysts for Engelhard in Edison, N.J. "And so the recession, in at least the first half of 1991, was delayed in the oil and catalyst industries because of the need to produce energy."

Although demand was high during the Gulf War, says Al Roeder, president of Criterion Catalysts, refiners were reluctant to replace catalysts. Criterion, formed in 1988, is a Houston-based joint venture between American Cyanamid and Shell. When the war ended rather abruptly, inventories of petroleum products were quite high, especially in the U.S., leading to competition and falling prices. As a result, oil companies are reporting tremendous losses, are operating at lower capacities, and are reluctant to spend the money to shut down operations to replace catalysts.

"I think to say [petroleum refining is] in a recession is very charitable," says Roeder. "And if it is hurting, then the catalyst industry hurts." Roeder does not see the situation improving much in the near future. "The effects of shutdowns and recession are much stronger than any growth from environmental requirements. The environmental impact is uncertain and the timing is clearly unknown."

FCCs, proprietary zeolite-based catalysts of a wide array of compositions, are the highest value refining catalyst market, and Davison Chemical, a division of W. R. Grace's specialty chemical business, is the leading producer, with a worldwide market share near 40%. Other major producers are Akzo; Engelhard; and Katalistiks, the FCC business of UOP, a 50-50 joint venture between Allied-Signal and Union Carbide formed in 1988.

Used to convert petroleum into oils, gasoline and other fuels, and lighter hydrocarbon fractions, cracking catalysts are needed to produce the desired distribution of certain products. This is because gasoline, once required to meet only a few specifications, now must meet several strict composition standards. Whereas FCC units tradi-

tionally produced about 30 to 35% of the gasoline pool, these units are being viewed now as a source of feedstocks for other processes. This means reduced levels of aromatics and light alkanes and increased yields of C_4 and C_5 olefins for use as less expensive feedstocks for the production of octane-building alkylates and oxygenates.

With the ban on lead additives in gasoline, aromatics became a major source of octane in gasoline. Restrictions now on aromatics are causing refiners to look for other sources of octane. What is desired are higher fractions of isobutylene for methyl *tert*-butyl ether (MTBE) or isoamylene for *tert*-amyl methyl ether (TAME) production, which in addition to their environmental benefits, increase octane levels. The demand for MTBE in reformulated fuels is expected to more than double over the next five years. Despite planned increases in MTBE production capacity, U.S. supplies are expected to lag demand by as much as 20%.

Richard Nozemack, vice president for FCC marketing at Davison Chemical, Baltimore, sees 1 to 3% market growth in refining catalysts in the U.S. in the next few years. Such a growth would depend on several factors, he says, including a turnaround in the recession. Eastern Europe and the former Soviet republics are looked upon by catalyst producers as potentially interesting, although currently uncertain markets. Engelhard has recently opened an office in Moscow.

In the Pacific Rim, where new refinery plant construction is planned or under way, growth in refining catalysts may reach as much 5 to 6% during the next five years. Growth in Europe is anticipated to be slightly faster than in the U.S., but not so fast as in the Pacific Rim, since reformulated gasoline is not yet an issue. However, "technology growth" overall will be dramatic, Nozemack says, because of a stiff need for technological improvements over the next five years. The challenge to suppliers is to provide solutions through "catalysis rather than capital," which means new catalyst technology that can be rapidly incorporated into existing equipment.

"There is a good opportunity to serve our customers by coming up with catalytic solutions that can use the existing capital or hardware in refineries," says Gustafson. "That's a much better solution than to spend lots of money. It takes a long lead time to [build] and right now

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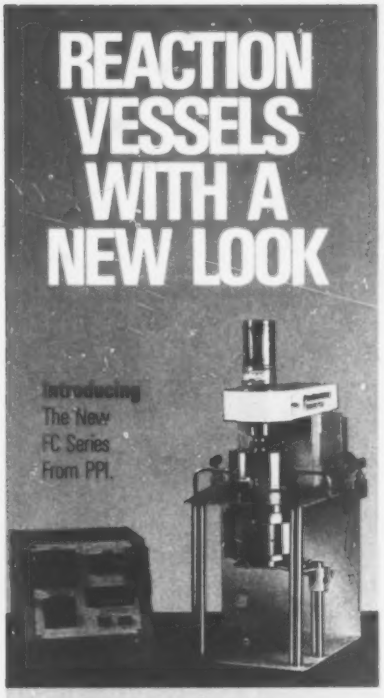

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I don't know how much lead time the industry will have if the regulations were to change." Catalyst suppliers are finding it necessary to work closely with refiners to produce catalyst formulations that perform optimally with different petroleum feedstocks and equipment, and that meet the desired product requirements.

Until about a year ago, FCC producers had been in a price war, explains Gustafson. It had been more than eight years since producers saw a price increase despite the fact that raw material, labor, and R&D costs were all increasing. Such costs, and tremendous overcapacity, have contributed to a history of rationalization and consolidation in the industry. Filtrol was absorbed by Akzo in 1989; ICI repositioned its catalysts business and sold its refinery catalyst business to Crosfield Chemicals, part of Unilever's Specialty Chemicals group, in 1990; and rumors persist about other companies reconsidering their positions, particularly in the FCC business. In 1991, Union Carbide and Allied-Signal each took a $60 million charge against earnings related to the UOP Katalistiks business.

About 18 months ago, Engelhard increased prices, Gustafson says, and in doing so lost a few percentage points in market share. However, the company believes it is in better shape as a result and sees itself as the number two supplier worldwide behind Davison Chemical, with Akzo as a close third. "Prices stabilized and have turned around, but they are not back to where they were even several years ago," he adds. "There is a continuing need to increase the price of catalysts so that the supplier has the money to invest in research and the tools in place to ensure that when industry needs it, we have the right products designed."

"We will see improvement in pricing, but it won't come fast enough to save all the companies out there," he continues. "The industry will continue to rationalize until it gets down to an acceptable number of profitable suppliers." FCC catalysts have relatively short product lives, and technological developments are crucial to staying competitive. Their value to refiners comes through increased activity, which leads to decreased catalyst consumption, and most efficient conversion of petroleum feeds. However, it is unlikely refiners will recover the investments made to meet regulations.

Like other suppliers, Engelhard has been introducing new FCC product lines to address refiners' concerns. Its Precision line, based on new zeolite technology, and Dimension line, based on new matrix technology, make up nearly 50% of Engelhard's sales over the past two to three years. Dimension is designed to deal with heavier fuel oils to give good selectivity against coke and gas production, whereas Precision is said to optimize gasoline yield and octane. Both also are said to maximize yields of light olefins such as isobutylene and isoamylene used to produce oxygenates. Gustafson adds that Engelhard is designing its next generation of catalysts to increase isobutylene yields as much as 100%.

To meet the demands for new catalysts, Davison started up its new 90 million-lb-per-year FCC catalyst plant in Lake Charles, La., in August 1991. It produces the company's new XP series, which has been under development for 10 years. XP catalysts are said to offer superior cracking of heavier, high-boiling petroleum fractions, or bottoms, with increases both in gasoline yield and octane. The company increased its catalyst capacity at the Lake Charles facility by 50%, after closing FCC production at its Cincinnati plant and consolidating these operations to Louisiana.

Davison has a new catalyst system, not based on the traditional faujasite zeolites used in FCCs, but rather on a proprietary zeolite, the structure of which the company will not disclose, that addresses many needs of reformulated gasoline. Similarly, Akzo manufactures lines of zeolite-based cracking catalysts for increased conversion and octane levels, low gas and coke production, and enhanced bottoms cracking. Akzo's CSC, or component selective cracking, catalysts are designed to

Value of world markets for catalysts to grow

$ Millions	1990	1995	Annual growth
North America	$2110	$2500	3.5%
Europe	1578	2571	10.3
Japan	837	1042	4.5
Other	1459	1775	4.0
TOTAL	$5984	$7888	5.7%

Source: Catalyst Consultants

give higher percentages of branched olefins in the C_4 to C_5 range while maintaining gasoline yields.

The restriction on aromatics is also anticipated to influence the operation of catalytic reforming units that in the past have produced about 30% of the gasoline pool. UOP is by far the largest producer of reforming catalysts, followed by Criterion. Reforming catalysts, which cyclize and dehydrogenate hydrocarbons, are generally combinations of platinum with iridium or rhenium on high-purity alumina supports.

Reformers are a major source of hydrogen in refineries. The hydrogen they produce is used in hydrotreating processes—namely, the hydrogenation of aromatics or olefins and the removal of contaminants such as sulfur, nitrogen, and metals in pretreating FCC feedstocks. Although the market for reforming catalysts may fall off in the U.S., growth may occur overseas where mandated phaseout of lead additives is leading to a need for higher octane gasoline. Although MTBE could be used, Europe has not yet put environmental standards in place for reformulated gasoline, but many anticipate that that may occur soon.

An increased hydrogen demand is being driven by U.S. mandates coming into effect in October 1993 for reduced sulfur and aromatics levels in diesel fuels. Sulfur levels will have to be reduced from an average of a few thousand parts per million to less than 500 ppm, says Roeder of Criterion. Low-sulfur regulations also are being adopted in Europe and Japan. The overall market may see a few percent growth per year, but the hydrotreating catalyst industry has been plagued by overcapacity problems. Criterion and Akzo are coleaders in the hydrotreating catalyst area, says Roeder, which contains many other smaller players.

Reducing sulfur with existing catalysts requires operating at high temperatures and pressures, but that is not entirely effective on aromatics, say those in the refining industry. Severe operating conditions decrease catalyst life while increasing the use of hydrogen and catalyst. A route to aromatics saturation might be through existing precious-metal hydrogenation catalysts found in the chemical processing industry. But refiners are reluctant to adopt technologies that are foreign to the refining industry, especially if they

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require new construction. Thus, refiners are looking for high activity, longer-life desulfurization, and hydrogenation catalysts that work in existing units.

Hydrotreating catalysts are generally base-metal catalysts such as molybdenum with cobalt or nickel on alumina or silica. Criterion has developed a new hydrotreating process called SynSat, whereas Akzo has its Ketjenfine product line. In addition, higher quality crude oils are being depleted, says Roeder, and refiners will be faced with crudes that have higher sulfur and metal contents, leading to increased catalyst usage. Engelhard offers its HPN process to selectively hydrogenate undesirable C_3, C_4, and C_5 components such as diolefins as pretreatment for alkylation, MTBE, and TAME feedstocks.

"It's a question as to what the strategy will be for running reformers in the future," says Gustafson. "I believe that the reformer's role is going to shift from being primarily an octane supplier to primarily a hydrogen supplier." One way is to run the units at lower severity to reduce the amount of aromatics produced, but with a reduction in hydrogen needed for other processes. Engelhard, like others, is developing isomerization catalysts that may offer an alternative.

Being very similar in composition to precious-metal-based reforming catalysts, isomerization catalysts are expected to be able to be used in reforming units without major changes to the units. And isomerization gives refiners a means to deal with the low molecular weight alkanes that may be regulated under vapor pressure standards. Isomerization catalysts can convert paraffins to isoparaffins, which have increased octane values, or to materials for MTBE and alkylate production. For example, n-butane can be converted to isobutane, which can then be dehydrogenated to produce isobutylene for MTBE. In both isomerization and FCC catalysts, there is increasing interest in shape-selective catalysts, both zeolitic and nonzeolitic materials, to control the products formed.

Through alkylation, lighter isoparaffins can be combined with small olefins to produce heavier, higher octane gasoline components. Since alkylates are desirable gasoline components, demand for alkylation catalysts is expected to increase. However, historically, this process has used large volumes of low-cost liquid acids such as hydrofluoric and sulfuric acids. Environmental and safety pressures are forcing refiners to replace corrosive, toxic, or hazardous materials with more benign or environmentally acceptable materials. In response, catalyst producers are looking for new catalytic routes to alkylation processes.

One such route targeted by many catalyst R&D efforts deals with solid acid catalysts that potentially could avoid operating costs related to handling hazardous materials. Catalytica along with Conoco, Du Pont's energy subsidiary, and Neste Oy, the Finnish oil company, have formed a joint venture to work toward commercializing Catalytica's new proprietary solid acid catalyst alkylation process. A pilot plant is planned to begin operating this fall at Neste's Porvoo research center in Finland. A key element of the process is that it allows existing liquid alkylation units to be converted to using the solid acid catalyst.

Chemical processing catalysts

Chemical catalysts play critical roles in processes in the chemical, petrochemical, petroleum, and pharmaceutical industries. The market for chemical processing catalysts is tied closely to end-use markets for the products they produce. As the chemical industry has been hit hard by the recession, so too have sales by catalyst suppliers. And competition and overcapacity in catalyst production, along with increasing raw material and R&D costs, are problems faced by the chemical processing catalyst industry.

Polymerization catalysts account for the largest dollar share of the chemical processing catalyst market at about 49%. With end-use markets for polymers down, sales in this area have been slow. Catalysts for oxidation (18%) and organic synthesis (16%) are the next largest categories, followed by synthesis gas catalysts (10%), and hydrogenation and dehydrogenation catalysts (8%). According to Catalyst Group, about 4% growth in chemical processing catalysts is anticipated overall in the U.S., although some markets will fare better than others.

According to Eugene Sanders, technical director of Calsicat, a division of Imcera's Mallinckrodt Specialty Chemicals subsidiary, Erie, Pa., the state of the economy "generally slowed down the usage of current catalysts. But it hasn't really slowed down R&D or the scaleup of catalysts for new processes. Our customers seem to be just as vigorous as ever in the pursuit of new [products]."

Gasoline reforming plant in Hawaii

Catalyst suppliers have to compete based on performance characteristics—high yields, lower operating costs, extended catalyst life, high quality, new or improved products, and attention to by-product and environmental concerns. R&D increasingly is being driven by the needs of specific customers. "More and more these days suppliers are getting away from developing one catalyst to serve a multicustomer market," says Sanders. "The competition from a performance standpoint is so keen that unless you can tailor a catalyst to fit a specific customer's needs, you are not going to be in the ball game."

Custom catalyst development is a growth area for many producers of catalysts for the chemical industry, as well as for the petroleum industry. Companies that have made their own catalysts in the past are said to be reconsidering this position during the current economic situation. This is leading to many more product development partnerships and closer, longer term relationships between customers and catalyst suppliers. It also means high R&D spending to support improvements in existing products as well as the development of new ones.

Environmental, health, and safety pressures on the use of hazardous reagents or in the production of by-products are leading to new catalytic routes to chemical products. In some cases, concerns have centered around the catalysts themselves when it comes to worker exposure or to the disposal of used catalysts. However, the desire for the most efficient catalyst may be at odds with the desire for less hazardous materials. Under these circumstances, customers often ask catalyst suppliers to take responsibility for the disposal or recycling of used catalysts.

Chemical processing catalysts are generally precious- and base-metal catalysts made on a proprietary basis. The types of catalysts and the variety of processes or products they are involved with are numerous. The result is a variety of suppliers ranging from those contributing to several markets to those with only one or two niche markets. Engelhard claims to offer the broadest range of chemical catalysts of any single manufacturer in the world. Contributing to its position was the acquisition of Harshaw, the base-metal chemical catalyst part of Filtrol-Harshaw, acquired in 1988.

The company supplies catalysts for products for a wide range of markets including automobiles, food, cosmetics, pharmaceuticals, fibers, soaps, detergents, construction, the environmental area, and packaging. "Our business is extremely leveraged in the automotive and construction industries," says William Staron, group vice president and general manager for chemical catalysts at Engelhard. "And on a global basis those industries were fairly depressed." Only Germany and the Pacific Rim have been isolated pockets of market strength, but this may not last.

In most areas, you will find a year-over-year drop of close to 15%," he

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adds. "[What that meant was] about a 10% drop on our overall performance in 1991." Soaps and detergents and environmental applications were growth areas worldwide in 1991 for the company, but the food and beverage industry remained fairly flat. "We see very little optimism for upturn and, if it does occur, it's going to be in the second half of 1992." However, because the catalyst industry traditionally lags the economy by six to nine months, adds Staron, "we won't realize any of those benefits in 1992."

With the polyolefins industry in a period of overcapacity, which has led to declining prices and profitability, markets for catalysts are also expected to be affected. Polymerization catalysts generally are transition-metal Zeigler-type catalysts or free radical initiators such as organic peroxides. Davison Chemical produces chrome-silica, rather than traditional Zeigler, catalysts for polyethylene production. In March 1990, the company announced the construction of a new catalyst plant in Curtis Bay, Md. The plant increased Davison's production of polyethylene catalysts by 50%.

Catalyst Resources, a Houston-based subsidiary of Phillips Petroleum, manufactures polymerization catalysts and, through its Houston subsidiary Aztec Catalyst, organic peroxides. Stephen Isaacs, senior marketing development manager for Aztec, says sales were up in 1991 over 1990. "Contrasting that, there has been a surge in raw material costs, and the company has not been able to recoup all of those increased costs." Aztec and Elf Atochem are among the major producers of organic peroxides.

Catalysts for producing polyurethane foams have been hit by the recession and the resultant slow markets for autos, furniture, and construction. Other pressures on the industry have been the removal of chlorofluorocarbon blowing agents and insulating materials in the foams, explains Bruce Ernst, polyurethane additives market manager of Air Products & Chemicals. This has required firms to develop catalysts to produce the same quality foams with different reagents.

Dehydrogenation catalysts for converting ethylbenzene to styrene also have been hard hit by depressed styrene markets. With demand low, styrene producers are avoiding costs by postponing shutting down operations and changing over catalysts, explains Roeder of Criterion Catalysts, one of the leading producers of styrene catalysts. "Everything is down about the market, so [Criterion] has a plant that is reasonably unoccupied."

Another major producer, United Catalysts, a Louisville, Ky.-based company owned by Süd Chemie of Germany, views the market situation a bit differently. "Styrene prices are very low, the market is very soft, and styrene plants are operating at reduced rates and trying to cut costs," says Robert Hartye, vice president for sales and marketing at United Catalysts. "In this kind of situation, where [customers] are looking to produce the lowest cost product, they are more interested in the highest selectivity catalyst that we can supply.

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"Fortunately for us, United Catalyst has the highest selectivity catalyst on the market, and so our market share has been very good during the past year and a half." With a big year in 1990, sales fell some in 1991, and this trend is anticipated to continue in 1992. "United Catalysts expects to have a better market share, but the total market will be reduced, and we hope there will be a rebound in 1993," Hartye says. "The company has also introduced a new styrene catalyst this year that produces less phenylacetylene, an undesired by-product." United Catalysts also supplies phosphoric acid catalysts used in the production of cumene. Because cumene goes into the production of phenol for plastics and resins, this market also was depressed this past year.

On a positive note, an exciting area in olefin polymerization is single-site metallocene catalysts, says Roger Singer, an industry consultant and head of Business Development Services in Villanova, Pa. "How these will impact older technologies remains to be seen," he says, "but for quite a while these catalysts have been the focus of many of the research departments in polyolefin producers worldwide." The area of metallocene catalysts, which consists of a broad range of catalyst compositions, is very competitive.

Metallocene catalysts are extensions of Zeigler-Natta chemistry using Group IV metals such as titanium and zirconium. However, depending on the structures and geometries of ligands on these single-site catalysts, they produce highly regular polyolefins with narrow molecular weight ranges. A better understanding and more control of the polymerization process through the design of the catalyst is expected to lead to enhanced polymers with greater uniformity in desired properties.

Dow Chemical is looking to launch its single-site constrained geometry catalyst technology in 1993. Although the technology is more than a decade old, advances made in the past five to 10 years have improved the stability, reactivity, and efficiency of these catalysts while maintaining their selectivity, says Brian Kolthammer, research associate in polyolefins at Dow. Mitsui of Japan is also actively involved in the metallocene area, as are other petrochemical and chemical companies worldwide.

Exxon Chemical's Exxpol catalyst process, its name for the single-site catalysts, is the first to be commercially offered. "I believe that metallocene single-site catalysts are going to find their way into almost every polyolefin process currently in use," says Mike Jeffries, Exxpol manager for Exxon Chemical in Houston. However, development costs have not been "insignificant," he adds.

In 1990, Exxon Chemical opened up a new 30 million-lb-per-year Exxpol plant in Baton Rouge, La., to produce a range of polyolefins. Products are being aimed at specialty markets, and the company is working closely with cus-

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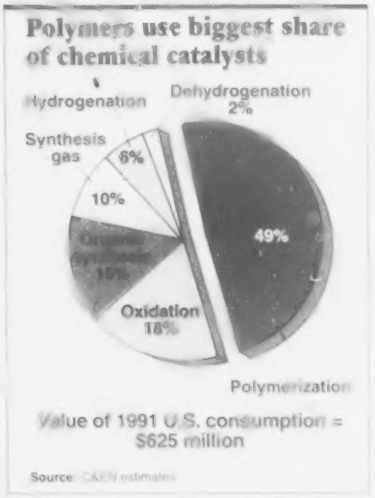

tomers to develop polymers for their needs. "The metallocene catalysts are as competitive, and potentially more competitive, than existing catalyst systems [in terms of manufacturing costs]," says Jeffries. "Our customer response has been very strong despite the weak economic climate."

After polymerization catalysts, oxidation catalysts and catalysts for organic syntheses are the next largest markets. Many large-volume chemicals such as sulfuric acid, nitric acid, ethylene oxide, and vinyl chloride are made using metal-oxide catalysts. Monsanto is the largest producer of vanadium pentoxide for the production of sulfuric acid. Shell, among others, produces silver-oxide catalysts for the synthesis of ethylene oxide. These, like other chemical markets, have been experiencing slow growth.

Catalytica is looking at a new process for oxidizing ethylene to produce acetaldehyde that substantially reduces chlorinated hydrocarbon by-products and the costs associated with their disposal or treatment. In commercial-scale tests, the company says its process provides equivalent yields, and can be used in existing plants with little or no modification. It is also applicable to oxidation of higher olefins.

Probably the only areas with any positive outlook are the smaller markets for synthesis gas, hydrogenation, and dehydrogenation catalysts. Synthesis gas catalysts are used in the manufacture of ammonia, methanol, and hydrogen. They are typically steam-reforming catalysts consisting of iron, nickel, cobalt, or molybdenum on a supporting material generally used to convert methane in the presence of steam to carbon monoxide and hydrogen. The reaction is a source of carbon monoxide and hydrogen for the production of methanol and hydrogen used to make ammonia. Another important factor in ammonia plants are carbon monoxide shift catalysts of copper-zinc or iron-chrome used to convert between water-carbon monoxide and hydrogen-carbon dioxide.

Synthesis gas catalysts are among the largest of United Catalysts' core businesses, and the company is a leading supplier of these. Overseas companies that came into the North American market in the mid-1980s contributed to overcapacity in the industry and caused United Catalyst's market share to slip. To regain market share, United Catalysts—like other synthesis gas catalyst producers ICI, Haldor Topsöe, and BASF—has been introducing new products with higher activities and greater stability for longer catalyst life.

However, synthesis gas catalysts are a mature area technologically, having been refined by producers for decades and having little room left for further advances. "I don't know when the consumption of these catalysts will catch up to capacity. Essentially all the new catalysts we are bringing out have longer and longer lives, so that decreases the market itself," says Hartye. "Extending catalysts' lives will cut down on the total replacement business market in those areas.

"As far as the total market, 1991 was an improvement over 1990. The catalyst market looked to be up about 10 to 15% in 1991, but there still is tremendous overcapacity in catalyst production for this area worldwide." Some long-term growth is expected, however. "In North America," he adds, "I don't see any growth in ammonia plants. The growth potential is more in the hydrogen and methanol areas." Catalyst Group estimates growth of about 1% per year in catalysts for ammonia and about 5% per year in methanol.

Demand for methanol is anticipated to increase significantly because of its

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use in making MTBE for reformulated fuels. Methanol is reacted with isobutylene or isoamylene to produce MTBE or TAME, respectively. "I see some of the [methanol] plants that have been shut down, restarting here in the U.S.," says Hartye, "and so I expect catalyst sales in the methanol area to improve, both in the near term and in the long term as requirements [for oxygenates] go up."

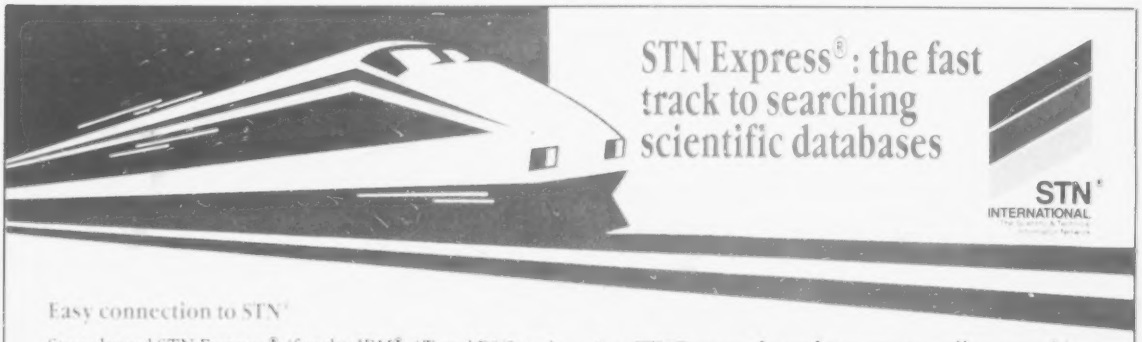
Another reason for growth in synthesis gas catalysts will come from the need for hydrogen to meet fuel desulfurization requirements. With less hydrogen being produced from reformers in refineries, an increase in construction of medium-size hydrogen plants is anticipated, leading to growth in the hydrogen area beginning almost immediately.

The market for dehydrogenation catalysts also is affected by the growth in demand for oxygenate feedstocks. Although the most inexpensive source of isobutylene or isoamylene is directly from the catalytic cracking unit, this is not expected to be enough to meet demand. Isobutylene can be produced by the dehydrogenation of isobutane to isobutylene. Thus, suppliers anticipate an increased demand for dehydrogenation catalysts. But there are no new dehydrogenation processes commercialized for isoamylene, and several companies are said to be working on this process.

Increased demand is leading to the construction of stand-alone MTBE plants in which about two thirds of the capital is in the dehydrogenation unit. United Catalysts' isobutylene dehydrogenation process is called the Houdry process, acquired, along with engineering partner Lummus Crest, from Air Products in June 1990. "At present there are only four MTBE plants based on dehydrogenation in the world, and all four of them are using the Houdry process," says Hartye. Competitors such as UOP and Phillips also offer processes and have signed up licensees.

"Because of the tremendous growth in MTBE, there has been a very large growth in our Houdry catalyst business, and already it's our second largest catalyst area," says Hartye. "And if MTBE remains the oxygenate of choice for the reformulated fuels, then we see a very, very large growth in this area for us." MTBE demand is also expected to grow in Europe, where it is currently being used as an octane enhancer, rather than for environmental concerns. United Catalysts is building a large catalyst plant in Louisville to supply the anticipated catalyst demands. Although its catalysts are chrome based, the company has worked out routes for recycling them to address disposal concerns.

Another category is hydrogenation catalysts, which may see some growth. Hydrogenation catalysts are used in petrochemical production, chemical synthesis, and fats and oils production. There are numerous competitors and, again, problems with overcapacity, particularly in the more mature fats and oils market. Engelhard is a leader in hydrogenation catalysts, says Staron, producing a wide range of base- and precious-metal catalysts used in a variety of applications. Calsicat also puts hydrogenation cata-



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Refining catalysts barely lead environmental ones

North American market ($ millions)	1990	1995	Annual growth
Petroleum refining	$ 730	$ 800	1.9%
Environmental controls	720	905	4.7
Chemical processing	660	795	3.8
TOTAL	$2110	$2500	3.5%

Source: Catalyst Consultants

lysts among its primary products, and Davison sells its Raney family of hydrogenation catalysts. United Catalysts also supplies hydrogenation catalysts for fats and oils as well as for use in petrochemical processing.

Hydrogenation catalysts can be base-metal or precious-metal catalysts depending on the type of hydrogenation reaction and the desired selectivity. Platinum group metal catalysts have high activities, high selectivities, and low consumption rates under mild reaction conditions. Base-metal catalysts containing nickel, cobalt, and copper chromite are used in hydrogenation reactions, as they are in dehydrogenation, and in hydrogenolysis to produce fatty alcohols. Engelhard is working to develop chrome-free hydrogenation catalysts with the same activity and selectivity as existing catalysts.

The market for edible fats and oils will remain at about the same level this year as last year, although that for inedible fats and oils, which go into consumable goods, will decline. As in other markets, the general trend is for more active and more selective catalysts, which contributes to reduced catalyst consumption. The market also is experiencing a decline in the consumption of fully saturated fats, and so catalyst suppliers are responding with more effective catalysts for partial hydrogenation.

In petrochemicals, selective hydrogenation catalysts are used to clean up C_2, C_4, and C_5 streams going into the production of ethylene, isobutylene, isoamylene, and alkylation feeds. In heavier streams, the desire is to remove diolefins without hydrogenating the desired products. Sanders says Calsicat has had some success with a noble-metal catalyst developed to clean up C_4 streams and is working on a modification of it for C_5 streams. Similarly, in C_2 streams, the goal is to selectively hydrogenate acetylene and not ethylene. In this area, Hartye says, "United Catalysts is by far the largest supplier with about 80% of the market.

"That area has been very good over the past couple of years for two reasons," he explains. "One is new plant startups, and the other is that the company came up with a very high selectivity bimetallic catalyst." Its proprietary catalyst was introduced a couple of years ago. "It is so much of an improvement that I would say the majority of the customers in this hemisphere have either already changed out or have made plans to change out to this new generation catalyst to take advantage of its much higher selectivity."

"This has made for two very big years for us in 1990 and 1991 for these catalysts," says Hartye. However, this market is slowing down as new plant construction slows. By the end of 1992 it is expected to fall off considerably because new plants are not envisioned in the next couple of years. "As the C_2 business slows down, United Catalysts is looking to come out with improved products to pick up some market share [in selective hydrogenation catalysts for heavier hydrocarbons]," he adds.

Related to ethylene production is a new calcium, nickel, and potassium mixed-oxide catalyst, reported in late 1990, that converts methane to C_2 hydrocarbons (C&EN, Nov. 26, 1990, page 8). This past November, Lawrence Berkeley Laboratory, where the catalyst was developed, joined in a cooperative R&D agreement with Orion Advanced Chemical Technology, based in Wilmington and part of the Ferruzzi-Montedison Group. The project aims to scale up the highly selective catalyst technology to see whether it is economically feasible on a commercial level.

Growth in emissions control

The catalyst market poised for the largest growth is emissions control—both for mobile and stationary sources. Automotive catalysts long have dominated the emissions control market.

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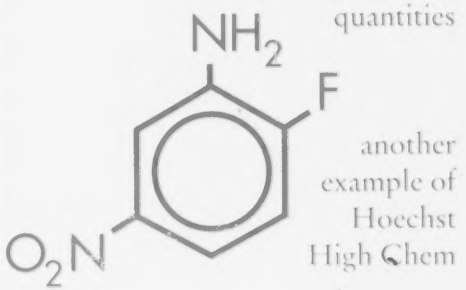

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However, increasing restrictions under the Clean Air Act are expected to open the market for pollution controls on stationary sources such as power and processing plants over the next 10 years. Catalytic technologies are aimed at controlling nitrogen oxides, sulfur dioxide, carbon monoxide, and volatile organic compounds (VOCs).

Automobile emissions catalysts are seeing both good and bad times in terms of market growth. In the U.S., growth is expected to be fairly flat, if not decreasing, because of the impact of the recession on automobile sales. However, offsetting slow growth in the U.S. are regulations coming into effect in 1993 in Europe that will lead to at least a doubling of the market there and about 15% growth overall.

Automotive catalysts are expected to grow from about 42 million catalytic units to about 49 million units worldwide by 1993, says Willem Groenendaal of Strategic Analysis, a Reading, Pa.-based market consulting firm. Europe, which accounts for about 9 million of the 42 million units currently sold, is expected to grow to about 20 million units by 1994 or 1995. This would make the European market about equal in size to that in the U.S.

About 75% of the value of auto emissions control catalysts is contributed by the precious metals, says Groenendaal. Precious metals in the platinum group, including platinum, palladium, rhodium, and ruthenium, are used in automotive, environmental control, chemical processing, and petroleum catalysts. Automotive catalysts, generally consisting of precious metals supported on ceramics or metals called monoliths, account for the largest usage of platinum group metals. Catalyst producers are always under pressure to produce more cost-effective products, and major targets are a reduction in the amount of precious metals used and an increase in the amount recycled.

According to the Department of the Interior's Bureau of Mines' figures for the first half of 1991, 9200 kg of platinum were sold in the U.S. for automotive uses. This market also consumed 1319 kg each of palladium and rhodium. Chemical processing catalysts used a total of about 1369 kg of all three metals, whereas petroleum catalysts used about 1782 kg of platinum and palladium.

The worldwide automotive catalyst

market is dominated by five competitors—Johnson Matthey, Allied-Signal, Engelhard, Degussa, and Davison Chemical. Johnson Matthey, based in Wayne, Pa., has the largest market share of about 30%. Both Engelhard and Allied-Signal's Automotive Catalyst Co. in Des Plaines, Ill., estimate their market shares to be between 20 and 25%. Degussa, with U.S. headquarters in Ridgefield Park, N.J., has less than 10% of the worldwide market, and Davison is a smaller player, supplying catalyst powders for coating auto catalyst monoliths.

"Engelhard is probably the most strategically located automotive catalyst manufacturer in the world," says James Healy, Engelhard's group vice president and general manager for environmental catalysts. The company has plants in North America, Europe, and South Korea, and in Japan through a joint venture, Nippon Engelhard Catalysts & Chemicals. None of Engelhard's competitors has a plant or joint venture in Japan to make catalytic converters, says Healy. Although U.S. automobile sales have been dropping, Engelhard says its market share has grown with sales to Japanese manufacturers in the U.S. And, Engelhard is in the process of expanding capacity threefold at its plant in Germany to meet European market needs and has bought out the other half of its German joint venture, Englehard Kali-Chemie GMBH.

Allied-Signal started up a manufacturing plant in early 1991 in Florange, France, and has already had to double capacity, which is scheduled to come on line in the first quarter of 1992. The company, which had sales of $179 million in 1991, has also built a new development facility in Toulouse, France, along with an engine testing and customer development laboratory. The next move will be to open a technical center in Japan by January 1993.

Although reformulated gasoline regulations are expected to have little direct impact on catalytic converter design, other pressures from automobile manufacturers and Clean Air Act regulations will affect their design. "All of our product development activity, whether it be stationary source or mobile source, is shaped by legislation," says Jerry Summers, technical director at Allied-Signal.

New provisions are requiring that the life of the catalytic converter be doubled to 100,000 miles. Three-way conversion catalysts currently operate as an oxidation catalyst to remove hydrocarbons and carbon monoxide, and as a reduction catalyst to remove nitrogen oxides. Although the number of replacement units sold will decrease, explains Healy, this may be offset by the larger size of the converters and their use of more catalyst. Catalysts also will have to be active or poison-resistant and temperature-stable over a longer period of time.

Another restriction being placed on automotive catalyst development is the reduction of hydrocarbon emissions during the first few minutes after an engine is started. During this "cold start" period, in which a converter is not yet hot enough to act catalytically, about 80% of a car's emissions occur. Davison, like others, is working on an electrically

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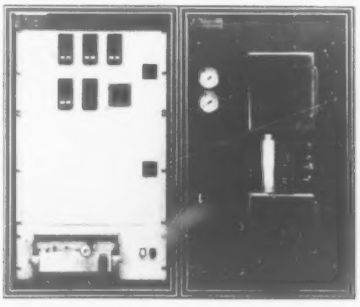

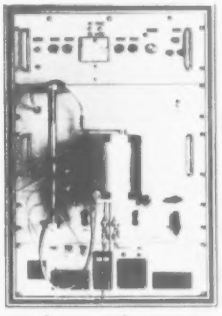

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heated version of its Camet metal monolith to address a more rapid control of emissions, says James Maselli, vice president for R&D at Davison. Allied-Signal and Engelhard also are looking at resistively heated converters.

Other approaches are a close-coupled catalyst, explains Healy, in which the converter is placed close to the engine or reducing the temperature at which the catalyst becomes active. Currently, typical under-floor catalysts become active at about 250 to 300 °C, he says. Yet another being worked on by Engelhard and Allied-Signal are systems to absorb or trap hydrocarbons from cold exhausts. When the system later heats up, hydrocarbons are released onto a hot, active catalyst. Engelhard is at the point, says Healy, where it can work with automobile firms to test the feasibility and limitations of its technology.

"Lean burn" applications to enhance fuel economy and lower hydrocarbon emissions also are presenting challenges for catalyst producers. Operating auto engines at an air-to-fuel ratio of about 20, or lean of the stoichiometric ratio of 14.7, increases nitrogen oxide levels. Traditional noble-metal catalysts are very ineffective at converting high levels of nitrogen oxides, says Summers, and so new technologies using materials such as zeolites are under development by Allied-Signal as well as by other companies. Catalyst producers also are looking at catalyst development for vehicles that run on alternative fuels, such as natural gas and alcohol mixtures, and have their own unique emissions profiles.

The market for controlling emissions from diesel engines is also growing, as new restrictions come into effect by 1994. Engelhard has focused specifically on this $150 million U.S. market for about two years, says Healy, and believes that its new proprietary catalyst developments will give the company a 40 to 50% market share in North America. This initial thrust has been so successful, he adds, that Engelhard is now focusing on Europe and Japan and has set up diesel engine labs in Germany and Japan, besides its lab in New Jersey, to support this effort. Smaller, yet growing, markets include off-road vehicles such as fork lifts and mining equipment.

Many catalyst producers are extending what they have learned in automotive emissions control to stationary source emissions control. There are four major targets for stationary emissions

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control—carbon monoxide, nitrogen oxides, VOCs, and sulfur dioxide—and different catalytic strategies involved. In addition, plants may consider other approaches such as process modifications or changes in formulations to prevent emissions. But for boilers, turbines, heaters, and other fuel-consuming units, suppliers say it is unlikely that catalytic controls can be avoided.

The U.S. market for industrial emissions control is estimated at only about $80 million in 1991, according to Catalyst Group, but it is forecast to grow as large as $1 billion by 2000. With the market still in its infancy, rapid growth will be driven largely by new regulations under the 1990 Clean Air Act in reducing pollutants related to ozone, smog, and acid rain. Along with the rapid growth in the market, the number of suppliers is expected to expand. California, with the most stringent standards in the country, leads in actual sales of stationary emissions controls, and producers watch what is happening there as a sign for what will happen elsewhere.

Healy sees two primary segments—small and large process industries looking for VOC reduction, and power generation units in utilities, industrial plants, or refineries. Both segments have potential growth of 30% or more over the next five years, once regulations are put into effect. A variety of other niche market applications are opening up in smaller boilers and cogeneration units or in small and medium-size spray painting, printing, and textile drying operations.

Currently, stationary emissions control technologies are much different from automobile emissions control. Development goals include high reduction activities, selectivity, and reaction efficiencies for specific contaminants, especially in the area of VOCs. Emissions control catalysts must also be resistant to poisoning from various contaminants as well as being durable and having long lives. Catalyst suppliers are seeing some demand by customers for service because plant operators are not necessarily interested in operating,

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maintaining, replacing, or disposing of emissions control catalysts.

A dominant technology is selective catalytic reduction (SCR) for nitrogen oxides formed at high temperatures in the combustion of fossil fuels. SCR processes react ammonia with nitrogen oxides in the presence of a vanadia-titania catalyst to form nitrogen and water. The Japanese lead in this technology, because regulations went into effect for stationary sources in Japan during the 1970s.

Similarly, Germany has adopted strict standards for coal-fired power plants and licensed much of the technology in use from the Japanese. The market in both Western and Eastern Europe is poised for growth if these standards are adopted by other countries as well. In the U.S., the SCR market may grow from a small base to a few hundred million dollars within a few years as regulations expand. Companies trying to gain position in the U.S. market include Engelhard and Davison Chemical.

Davison's Synox technology is a base-metal catalyst system aimed at nitrogen oxide removal in utilities while trying to avoid SO_2 conversion to SO_3. Like other SCR catalysts, it is based on vanadium on titania and operates at temperatures between 300 and 400 °C. But, unlike typical SCR catalysts, the company says it has a higher activity and selectivity. The company also markets a system developed by Noxso Corp., in which W. R. Grace holds an equity position. This technology simultaneously removes nitrogen oxides and sulfur oxides from utility flue gases. It is based on a continuously regenerable sodium carbonate on alumina adsorbent. In fact, a majority of sulfur oxide removal systems are based on adsorbents, and effective catalytic systems have yet to be developed.

Davison's Camet product line of metal monolith catalysts includes a precious-metal system for simultaneously removing nitrogen oxides and carbon monoxide through an oxidation process. However, in general, precious-metal catalysts cannot handle all stationary emissions problems well since they are easily poisoned by sulfur. Therefore they are used in niche applications. Davison's catalysts are targeted at engine exhausts, gas turbine preburners, cogeneration plants, and VOC solvent incineration, among other ap-

plications. Engelhard says it has developed a carbon monoxide oxidation product that tolerates high sulfur levels as well as other precious-metal emissions catalysts aimed at VOC control.

Engelhard is a small player in the SCR market, but it is taking another approach toward nitrogen oxide reduction using its proprietary zeolite technology in some smaller applications, such as process boilers and cogeneration units. An advantage of the zeolite catalysts is that they have fewer disposal problems, says Healy, and can operate at temperatures about 100° C higher than SCR catalysts. The ability to operate at higher temperatures avoids costs associated with heat exchange systems needed for SCR.

Another approach to nitrogen oxide reduction is targeted at its initial production. Catalytica is working with Tanaka Kikinzoku Kogyo of Japan in developing a catalytic combustion technology for electric power generation by natural-gas turbines. The proprietary technology has demonstrated emissions well below current and proposed regulatory limits without any exhaust gas after treatment, says Catalytica. Nitrogen oxide emissions have been reduced to less than 1 ppm, and carbon monoxide and hydrocarbon emissions have been reduced to less than 10 ppm.

Engelhard calls its catalytic combustion technology "catathermal combustion." These precious-metal catalytic systems are aimed at getting the same fuel efficiency out of a turbine, says Healy, but while operating at a temperature below 1500° C. It is above that temperature that atmospheric nitrogen reacts to form nitrogen oxides.

Allied-Signal recently has started its own efforts in industrial emissions controls, but it is not a player in the SCR market. In 1990, its industrial catalysts division had sales of about $1 million, but the company is anticipating reaching sales of about $40 million by 1995. One area it is focusing on is VOC controls. Since emissions-control catalysts containing precious metals alone would be strongly poisoned by halogens and insufficiently active, Allied-Signal has developed a new family of catalysts. Its halohydrocarbon destruction catalysts, a combination of base and precious metals, will convert a wide range of halogen-containing hydrocarbons to harmless products, says Summers.

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